THE STRUCTURE OF TRANSITIONAL ANORTHITE: A COMPARISON WITH PRIMITIVE ANORTHITE

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The structure of a volcanic transitional anorthite with diffuse type-"*c*" reflections has been refined three-dimensionally. It is observed to have similar lattice dimensions to low (primitive) anorthite. Its atomic coordinates are insignificantly different. There may be some importance in the variation of its Ca thermal parameters from those of the low-temperature structure, although at this stage in the work all that can be said with certainty is that transitional anorthite is made up of quenched-in domains of primitive anorthite occurring in an anti-phase relationship such that the perfectly ordered Al/Si alternation is not disturbed. There is no evidence of other disorder in the structure.

Introduction

Laves and Goldsmith (1951a, b (reprinted 1954a)) showed that certain important variations in the X-ray diffraction pattern of anorthites depend on the temperature of origin. They recognised that two different processes were responsible for the diffuseness of "*b*" and "*c*" reflections (see classification in Table 1), and suggested that the "*b*"-types were associated with Al/Si order. They showed that "*c*" reflections are only observed in the presence of "*b*", and become more diffuse the higher the temperature of quenching. In a more complete account of this work (Laves and Goldsmith (1954*b*)) they gave evidence of the relatively rapid change of "*c*"-reflection diffuseness with thermal treatment and argued that it could not be due to Al/Si order-disorder effects; hence they attributed it to Ca. They advanced the hypothesis

Table 1. Classification of anorthite reflections (after Gay (1953)).

Type	Indices	Primitive Anorthite	Transitional Anorthite
"*a*"	$h+k$ even, l even	sharp, strong	sharp, strong
"*b*"	$h+k$ odd, l odd	sharp, weak	sharp, weak
"*c*"	$h+k$ even, l odd	sharp, medium	diffuse
"*d*"	$h+k$ odd, l even	sharp, very weak	absent

of anti-phase domains to explain the diffuseness and concluded that the degree of diffuseness depended on domain size. They did not apparently recognise that the distinction between subcells which makes anti-phase domains possible depends essentially (in strongly-bonded structures) on geometrical alternations of the framework, which are not necessarily caused by particular ordering patterns (see Megaw (this volume)), and hence their discussion of the nature of the domains has to be modified in the light of more recent work.

Concurrent with the work of Laves and Goldsmith was that of Gay (1953, 1954) and Gay and Taylor (1953) who recognised the anorthites of temperature-origin above 1150 °C as transitional between primitive and "body-centered" anorthites and concluded that the sharp "*b*" reflections were an indication of Al/Si order. Later work (Laves and Goldsmith (1955), Goldsmith and Laves (1956)) deal with the possibility of obtaining Al/Si disorder by rapid crystallisation of a glass or by low-temperature hydrothermal treatments, but such disordered states are metastable only.

More recently Kempster, Megaw and Radoslovich (in press) and Megaw, Kempster and Radoslovich (in press) have studied the structural details of low-temperature primitive anorthite in three dimensions. They find it to be completely ordered with respect to Al/Si and describe four anorthite subcells which are compositionally identical but whose atomic coordinates are slightly different from one subcell to the next. The pattern of order is one of perfect Al/Si alternation, the Si sites in two of the subcells being occupied by Al in the other two.

The present work was undertaken to precisely determine the differences between primitive and high-temperature transitional

anorthite. Megaw (1960) had presented a model based on stacking faults and antiphase domains which could account for the diffuseness of "c" spots, and her prediction (Megaw (1961)) was that the structures would be essentially identical in their other features. This has proven substantially correct.

Three-dimensional structure analysis of transitional anorthite

The specimen chosen for this study was a transitional anorthite supplied by Dr. P. Gay and taken from a Miyaké (Japan) volcanic lava. The chemically determined composition is 99.1 mol.% An (Gay (1953)). The degree of diffuseness of the type-"c" reflections (~ 6 on the scale of Laves and Goldsmith (1954b)) indicates a crystallisation temperature of ~ 1400 °C for this material.

The cell dimensions of the Miyaké anorthite were assumed to be the same as those for primitive anorthite for two reasons: (1) measurements of d_{010}, α^* and γ^* disclosed differences which were non-significant (Table 2), and (2) other workers (Goodyear and Duffin (1955), Laves and Goldsmith (1955), Smith and Gay (1958)) found it impossible to clearly distinguish dimensional differences between natural low- and high-temperatures forms of anorthite. The structure is clearly centrosymmetric as shown by both the N(z) test (Howells, Phillips and Rogers (1950)) and the P(y) test (Ramachandran and Srinivasan (1959)) in Figures 1a and 1b. The result of the P(y) test on primitive anorthite is also given here (Figure 2) to resolve the uncertainty about its centrosymmetry (Kempster, Megaw and Radoslovich (in press)) and to compare it directly with that on transitional anorthite.

Table 2. Comparison of anorthite lattice parameters.

	Primitive An*	Transitional An (with method used)	
d_{100}	7.3492 ± .0005 Å		
d_{010}	12.8406 ± .0005 Å	12.852 ± .010 Å	(graphical extrap.)
d_{001}	6.3594 ± .0005 Å		
α^*	85°53.3′ ± 01′	85°51′ ± 05′	(precession photo.)
		85°54′ ± 02′	(graphical extrap.)
β^*	64°01.8′ ± 01′		
γ^*	87°06.2′ ± 01′	87°08′ ± 05′	(precession photo.)

* Cole, Sørum and Taylor (1951).

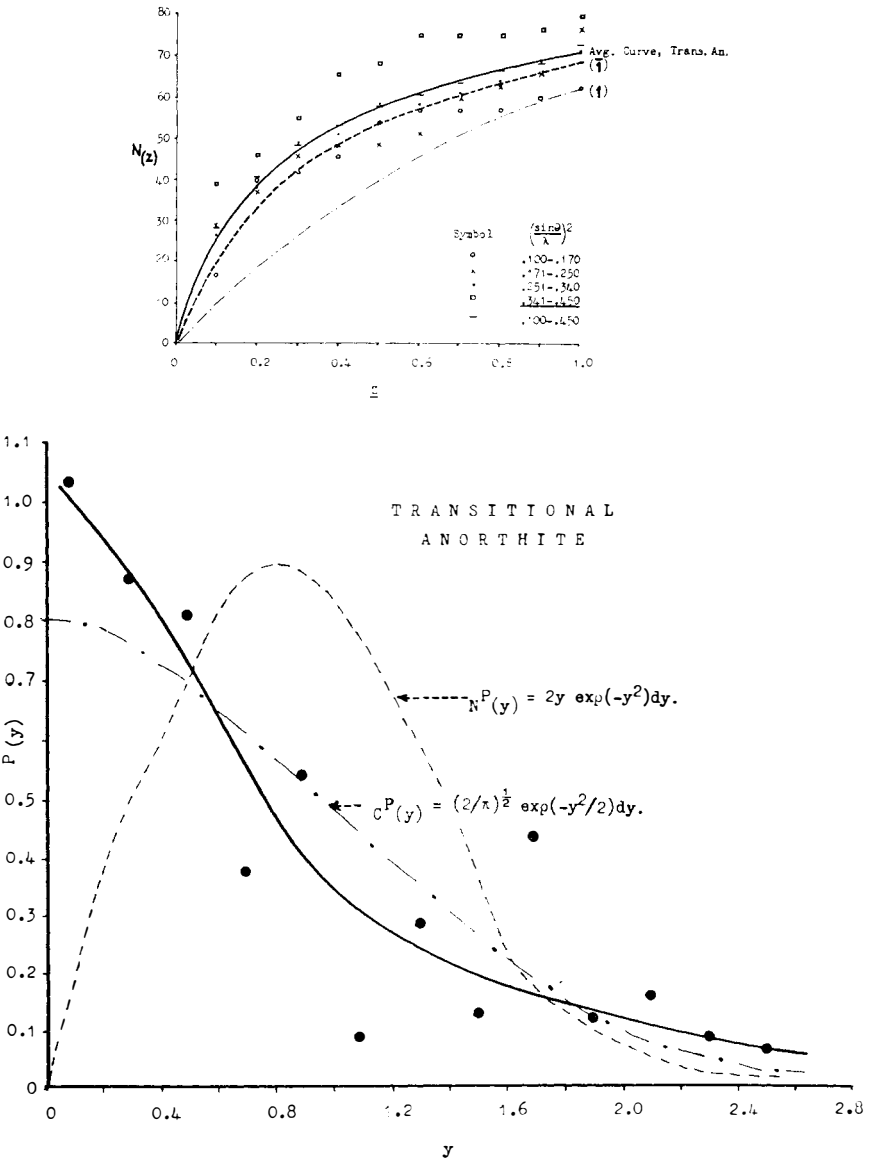


Figure 1. Statistical tests showing the centrosymmetry of the Miyaké transitional anorthite. 161 0*kl* reflections were used in the calculation of the experimental points.

a. The $N_{(Z)}$ test of Howells, Phillips and Rogers (1950).

b. The $P_{(y)}$ test of Ramachandran and Srinivasan (1959).

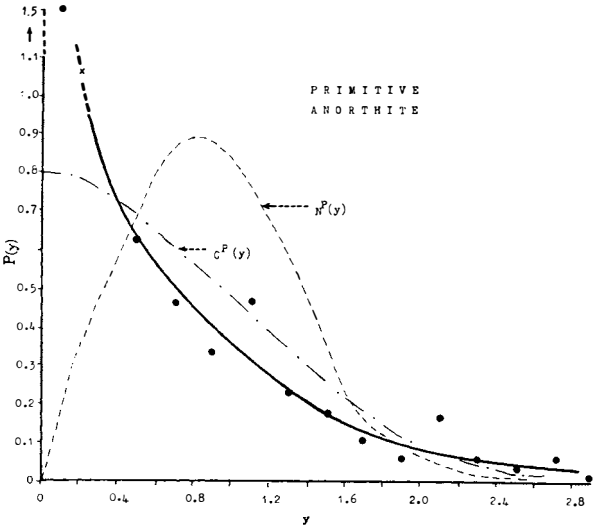


Figure 2. The results of the P(y) test on primitive anorthite, conclusively demonstrating its centrosymmetry. Experimental points are based on 237 "a", "b", "c" and "d" reflections from the zero-level a-axis Weissenberg photograph (Kempster (1957)).

Although the type-"c" reflections for the triclinic Miyaké feldspar are quite diffuse, their presence shows that the space group is $P\bar{1}$; however *because* they are diffuse, their intensities are for practical purposes unmeasurable, and they are ignored in this refinement. The "d" spots, which are extremely weak in primitive anorthite, are apparently absent in transitional anorthite, although they, too, may be diffuse and simply unobservable.

Approximately 2200 type "a" and "b" reflections were gathered from MoKα Weissenberg photographs of the $0kl$–$5kl$ levels. The intensities were visually estimated from standard multi-film packs and were corrected for extension-contraction effects on a family of experimentally derived curves. Absorption has been ignored, although at a later stage it is expected that corrections will be made to affirm the final details of thermal parameters. Corrections for the Lorentz and polarization effects were carried out on EDSAC II (as were most of the calculations involved in this study), and the layers of data were placed on an absolute scale by scaling to the primitive anorthite structure. A three-dimensional automatic refinement program, using a

difference Fourier synthesis method for calculating parameter shifts (Wells (1961)), was employed, and to date some 18 cycles have been completed. The first 10 were concerned only with refinement of atomic coordinates. The remaining 8 allowed the isotropic temperature factors and the coordinates to refine simultaneously. Extinction effects noted in the primitive anorthite analysis were avoided by omitting F_o's for $(\sin\theta/\lambda)^2 < 0.1$.

The authors have chosen not to present the coordinates, bond lengths and interbond angles at this time, because the refinement is not yet complete. Only such information as is useful for a comparison of the features of this structure with that of primitive anorthite is given.

A comparison of transitional and primitive anorthites

It has been stated (Laves and Goldsmith (1954a, b; 1955)) that the anorthite type-"*a*" reflections are due to its fundamental feldspar structure and that the type-"*b*" reflections are controlled by Al/Si ordering within the tetrahedral framework of the structure (see also Gay (1954)). When these spots alone are considered, transitional and primitive anorthites are seen to be very similar indeed. Table 3 gives the R'-factors determined between the observed structure amplitudes (F_o's) of the "*a*" and "*b*" reflections of the two anorthites. The mean value of 10.2% is less than the final value $R = 11.1\%$ for primitive anorthite and the current value $R = 10.9\%$ for transitional anorthite.

This can be interpreted as evidence that the refinement of transi-

Table 3. R'-factors calculated for type "*a*" and "*b*" F_o's of transitional anorthite and primitive anorthite.

(Unobserved F_o's are omitted from the analysis)

Layer of data	$R' = \frac{\sum \lvert \lvert F_{T.A.} \rvert - \lvert F_{P.A.} \rvert \rvert}{\sum \lvert F_{T.A.} \rvert} \times 100\,\%$
$0kl$	10.5
$1kl$	10.7
$2kl$	10.1
$3kl$	9.3
$4kl$	10.4
$5kl$	10.0
mean	10.2

Table 4. Average atomic coordinate shifts for transitional anorthite from the primitive anorthite positions.

Atom	Fraction of the unit cell edge, $\times 10^{-4}$		
	$\lvert\overline{\Delta_x}\rvert$	$\lvert\overline{\Delta_y}\rvert$	$\lvert\overline{\Delta_z}\rvert$
Ca	2	5	11
Al/Si	5	4	6
O	8	4	12

tional anorthite will have to proceed to somewhat greater accuracy before significance can be attached to parameter shifts. In any case it will be difficult to determine whether or not any small observed differences are meaningful. In view of the different thermal history of these feldspars certain variations in domain size are to be expected, as evidenced by diffuseness of the "*c*" and "*d*" reflections [1].

The predictions of similarity of the structures were well made as far as the atomic coordinates of the two are concerned. Table 4 indicates that the coordinate shifts for transitional anorthite from the original primitive anorthite trial structure are non-significant. This means that the Miyaké specimen has a fully ordered Al/Si distribution, the tetrahedral cations obeying Loewenstein's (1954) aluminium avoidance rule.

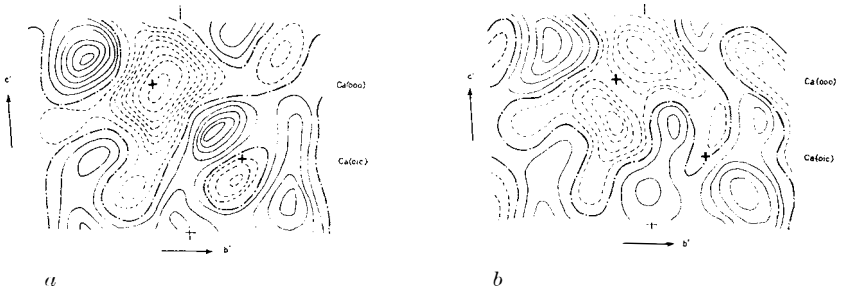
However, in the thermal parameters there is a very sharp contrast between the B values of the pairs of atoms Ca(*oo*, *zi*) and Ca(*zo*,*oi*) (Table 5). A contrast of the same kind was found in (low) primitive anorthite, but it was not quite so marked. It may be that the values for the low anorthite structure are not fully refined; but if they are, the

Table 5. Isotropic temperature factors (B_{calc} values) for atoms in the two anorthites.

Atom	Primitive An	Transitional An*
Ca(*ooo*,*zio*)	1.0	~1.8
Ca(*oio*,*zoo*)	0.3	~0.3
Al/Si	0.2	0.3
O	0.6	0.7

* Not fully refined.

[1] An admittedly rough correlation of the intensities of transitional anorthite diffuse-"*c*" and primitive anorthite sharp-"*c*" reflections has led to the conclusion that the integrated intensities for the two are quite similar.

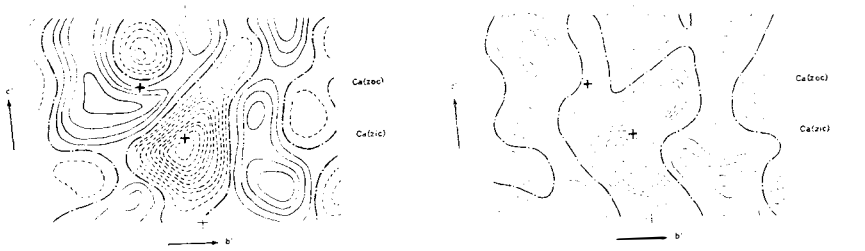


a *b*

Figure 3. The [100] projection of the $(\varrho_o - \varrho_c)$ electron density distribution in the environment of the transitional anorthite Ca(*ooo*) and Ca(*oic*) atoms.
Negative contours are given as broken lines, zero contours as chained lines, and positive contours as continuous lines. The contour interval is $\sim$0.25 e.Å^{-2}.

a. Primitive anorthite parameters. B_{calc} for Ca(*ooo*) = 1.0, for Ca(*oic*) = 0.3.
b. Refined parameters, B_{calc} for Ca(*ooo*) = 1.8, for Ca(*oic*) = 0.4.

difference between the low and transitional anorthites is significant. The $(\varrho_o - \varrho_c)$ maps of Ca environments (Figures 3*a* and 4*a*) show the deep negative trough in which Ca(*ooo*) and Ca(*zic*) are situated when $B_{\text{calc}} = 1.0$ and the parameters are those of primitive anorthite. They are in contrast to the maps in Figures 3*b* and 4*b* when the improved B values are used (with refined atomic coordinates). These results are to be regarded as preliminary, since further refinement is intended. The new value $B_{\text{calc}} = 1.8$ for Ca(*oo, zi*) is approximately that of K in sanidine and Na in low albite.



a *b*

Figure 4. Same as Figure 3 except that the environments of Ca(*zoc*) and Ca(*zic*) are shown.

a. Primitive anorthite parameters. B_{calc} for Ca(*zoc*) = 0.3, for Ca(*zic*) = 1.0.
b. Refined parameters. B_{calc} for Ca(*zoc*) = 0.2, for Ca(*zic*) = 1.7.

The meaning of the difference between the two structures (if real), or between the two types of Ca atom in the same structure, is not clear, and at the present stage it is considered unwise to attach much significance to it. Adding to the uncertainty is the degree to which anisotropy—thus far ignored—is influential (see Figures 3*b* and 4*b*). Whether it is thermal motion or structural strain at or near the domain boundaries that causes the observed effect is in any case indeterminate until a further detailed study of the distribution of intensity of diffuse-"*c*" reflections gives insight to the spatial disposition and nature of these quenched-in domains.

Conclusions

The transitional anorthite structure is essentially that of primitive anorthite. No differences in atomic coordinates can be considered significant, although the thermal parameters may be. Domains of primitive anorthite occur in an anti-phase relationship such that the perfect Al/Si alternation is not interrupted at domain walls; there is no evidence of other disorder. The present work throws no further light on the relationship of domain size to quenching temperature, nor (as yet) on the nature of the domain boundaries, but shows unambiguously what the structure is *within* the domains.

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